THESIS

for the Degree of

DOCTOR OF SCIENCE.

on

THE PHYSICAL PROPERTIES OF SOLUTIONS OF OPTICALLY - ACTIVE BASES WITH AN ENANTIOMORPH PAIR OF ACIDS.

by

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Since Pasteur discovered how to resolve racemic acid by means of an optically active alkaloid, systems consisting of a pair of optically active stereoisomers and an independent optically active substance have been of interest theoretical and practical.

The development along this line of the principles of asymmetry and enantiomorphism has lead to other methods of separating the active isomers.

Thus Marckwald and Mc.Kenzie (1) have shown that the rate of esterification of l. Menthol by l. Mandelic Acid is slower than that of l. Menthol by d. Mandelic Acid. Further, it has been shown that the saponification of l. Menthyl d. Mandelate by alcoholic potash is more rapid than that of l. menthyl l. Mandelate, a similar behaviour being found in the case of the mandelates of l. Borneol.

Also, by choosing suitable conditions, and employing an/

(1) Marckwald & Mc.Kenzie Ber. 34. 469. 1901
Mc.Kenzie. J.C.S. 85. 1249. 1904
McKenzie & Thompson - 91 789. 1907
McKenzie & Müller - - 1814. 1907

an insufficiency of alkali for complete saponification, either a dextro or a laevo salt may be obtained from either l. Bornyl, r. Mandelate or l. Menthyl r. Mandelate. Generally, the former gives a l. potassium salt and the latter a d. salt.

In the original case of Pasteur's resolution there is a difference of solubility in the case of the enantiomorphs, and, indeed, this is the property which enables separation to be effected. In confirmation of this, we have the work of Kipping and Pope [1] by which they showed (1) that if d. glucose was added to a solution of sodium chlorate, an excess of dextro-rotatory crystals separated out on crystallisation, and (2) that if the same independent optically active substance was added to a solution of sodium ammonium racemate, the deposit formed was found on recrystallisation to consist principally or entirely of the d. tartrate. Quite recently, however, [2] they have shown that this result is obtained without the presence of d. glucose.

(1) J.C.S. 73. 606. 1898.
Proc. Chem. Soc. 14. 113. 1898.

(2) J.C.S. 95. 104. 1909.

Van 't Hoff, to whom the theoretical development of the subject is largely due, suggested that d. and l. isomers should have different solubilities in an optically active pure solvent; but Goldschmidt and Cooper [1] found that the solubilities of d. and l. caroxim in active limonen are identical; subsequently Cooper [2] showed that sodium hydrogen d. and l. tartrates have the same solubility in d. glucose solution.

H. O. Jones [3] similarly found that the solubilities of d. and l. camphor, and of d. and l. camphoroximes in d. pinene and in l. amyl bromide were the same.

Tolloczko [4] was unable to effect separation of d. and l. Tartaric acid by using active amyl alcohol to dissolve racemic acid.

Ranken and Taylor [5] examined the physical properties - density, viscosity, and specific conductivity - /

(1) Zeit. Phys. Chem. 26. 711. 1898.

(2) Amer. Chem. Jour. 23. 253. 1900.

(3) Proc. Camb. Phil. Soc. 14. 27. 1907.

(4) Zeit. Phys. Chem. 20. 412. 1896.

(5) Proc. Roy. Soc. Edin. XXVII. 172. 1907.

conductivity - of solutions of the Potassium Tartrates and of the Tartar Emetics, both alone and in presence of an independent optically active substance - cane sugar (and in one set of observations - Maltose). The results showed no difference of properties (except one) among the optically active and racemic forms either alone in solution, or in presence of the optically active substance. The exceptional case was that of viscosity, and it was found that the racemic form always gave a smaller viscosity than either of the optically active forms. The differences were small and increased with the concentration.

This is undoubtedly to be ascribed to the existence of r. molecules in the solution.

Investigations have also been made to ascertain whether any difference exists between the rates of inversion of cane sugar by the d. and l. varieties of the same acid. Thus Emil Fischer [1] employed d. and l. camphoric acids; and Caldwell [2] employed the β sulphonic acids of d. and l. camphor.

In/

(1) Zeit. Physiol. Chem. 26. 83. 1898.

(2) Proc. Roy. Soc. 74. 184. 1904.

In both of these cases the rates of inversion were found to be identical.

Bredig and Balcom[1] studied the decomposition of d. and l. camphor carboxylic acids in d. and l. limonen solution, and the four reaction curves when plotted, appeared identical within the limits of error.

On the other hand, Bredig and Fajans [2] investigated the decomposition of the same acids - not in an indifferent optically active medium but in presence of an optically active base. In this case, Nicotine, either alone, or diluted with an indifferent substance, was taken; and it was found that the d. acid was decomposed more rapidly than the l. acid.

Another method of investigation has been adopted by A. W. Stewart [3] who has examined the absorption spectra of the tartaric acids, and finds that the spectra of the d. and l acids are identical. At low concentrations, the apectrum of a/

(1) Ber 41. 740-751. 1908.

(2) Ber. 41. 752-763. 1908.

(3) J.C.S. 91. 1537. 1907.

a solution of racemic acid is the same as that of either of the active forms; but at high concentrations (over 14%) the racemic solution shows greater absorption. The curve of oscillation frequencies of racemic acid gradually merges into that of the d. and l. curve, and the spectrum of a dilute solution of racemic acid is identical with that of an equimolecular mixture of d. and l. acids. He concludes that above 14% concentration, a solution of racemic acid contains racemic molecules.

Stewart[1] has also investigated the dielectric constants of active and racemic compounds, and finds the effect of the spacial arrangements of atoms on this property not clearly marked. In one case, however, the active isomer was found to possess a stronger absorptive power than the racemic form.

Referring again to the work of Ranken and Taylor (loc. cit) in the course of which they found that the viscosity of solutions of the racemic form of certain substances was less than that of solutions of the optically active isomers, it was subsequently shown by Dunstan and Thole[2] that the/

(1) J.C.S. 93. 1059. 1908.

(2) J.C.S. Trans 93. 1815. 1908.

the viscosities of d. and l. Tartaric acid in solution are identical, but that the viscosity of r. solutions is less, the divergence from the curve of the optically active form increasing with the concentration. The differences are small throughout.

Finally, it may be mentioned that Byk[1] observed that alkaline solutions of copper tartrate and of copper Racemate differ slightly in colour.

The present investigation was undertaken, on the suggestion of Dr. Taylor, to find whether any differences could be found in the physical properties of solutions of the optically active and racemic forms of a substance in presence of an independent optically active substance, in a case where chemical combination was known to take place.

(1) Zeit. Phys. Chem. 59. 682. 1904.

The acids employed in the investigation are dextro and laevo Tartaric acids and Racemic Acid.

The first two were obtained from Kahlbaum and the last from Merck.

None of these were recrystallised, as they were found to be sufficiently pure.

The d. acid gave on analysis :—

	I.	II.	Theory.
C	31·98	31·89	31·99
H	4·028	4·031	4·031

The three acids were titrated with standard baryta, and it was found that 10 c.c. of this solution neutralised the following weights of the acids:-

Dextro Acid (Sample I.)	·00658 grams
" " (Sample II)	·00659 "
Laevo Acid	·00663 "
Racemic Acid	·00657 "

The base used in the first instance was d. Quinidine, but it was found impossible to obtain measurements of even 3% solution of either d. l. or r. tartrate, owing to the readiness with which the solutions deposited crystals.

I found, for instance, that a 2% laevo solution deposited crystals in an hour, and a 1·5% solution behaved similarly in 3 or 4 hours. The laevo solutions were the most troublesome, and the dextro solutions the least troublesome, in this respect; and even dilute solutions (·5%) could not be kept for any length of time.

These crystals were not examined in any way.

Notwithstanding the difficulty mentioned, measurements were made of the density and refractive index of a series of solutions of concentrations varying from ·5% to rather less than 3%.
[See also Hädrich, Zeit. Phys. Chem. 12. 482]

Two samples of d. Quinidine were used: the first, obtained from Merck, gave

M.P. 170°·5 - 171°·5

This sample was recrystallised from absolute alcohol, and was then dried, first in the air and then in a desiccator over concentrated H_2SO_4. At this stage, it had an efflorescent appearance. It was then completely/

completely dried in a steam bath (6 hours). The whole of this process was then gone through a second time, and the dried final product gave

M.P. 169° - 170°·5

The second sample was simply dried in an air bath; the dried substance gave

M.P. 169° - 171°

Lenz gives M.P. 171°·5 (cor.) (Zeit. Anal. ch. 27. 571)

The formula of Quinidine is $C_{20}H_{24}N_2O_2$, and, as it was completely dehydrated before use, the salts were made up in the following proportions of base and acid:-

For Racemate 2 $C_{20}H_{24}N_2O_2$ and $(CHOH.COOH)_2$ H_2O

For d. and l. 2 $C_{20}H_{24}N_2O_2$ and $(CHOH.COOH)_2$.

From the formula weights of base and acid, factors were deduced by which, when the weight of base is given, the equivalent weight of acid is at once found.

Some of the d. tartrate was prepared by dissolving equivalent quantities of acid and base, crystallising out the solid, and air-drying it.

(1) On heating ·5593 grams of this salt first in a steam oven for two hours and then in an air oven at 120° till the weight became constant, it was/

was found that the loss of weight was ·0139 gr. The loss of water was therefore 2·48%. Hesse (Annalen 146. 357) gives 2·55 and 2·41. (Theory 2·21% for $1 H_2O$).

(2) One solubility determination was made:- by shaking up salt and water in a thermostat at 25°, pipetting through a filter a small quantity of the solution and evaporating it cautiously to dryness. The residue was then heated for three hours in a steam bath and then in an air oven (120°) to constant weight. 1·8512 grs. of solution gave ·0479 gr. residue. The solubility was therefore 2·586% of solution. Hesse (loc. cit) gives 2·58% at 15°

The base subsequently adopted was l. Menthylamine. This was found to give stable Tartrate solutions of much higher concentration than d. Quinidine.

l. Menthylamine is a liquid (B.P. 204°) with a characteristic odour, and cannot be left exposed to the air as it rapidly unites with carbonic anhydride to form a solid compound.

This base was obtained from Schuchardt.

It was pointed out by Tutin and Kipping (~~Proc~~ J. Chem. Soc. 85. 65.) that l. Menthylamine prepared from l. menthone either (1) by reduction of its oxime, or (2) by heating it with ammonium formate, is a mixture of 4 optically active isomeric bases. These are all laevo bases, and for the purposes of comparison, as proposed in this research, this fact is not of consequence.

The formula of Menthylamine is $C_{10}H_{21}N$, and the salts were made up in the following proportions of base and acid:-

For Racemate 2 $C_{10}H_{21}N$ and $(CHOH.COOH)_2 . H_2O$

For d. and l. 2 $C_{10}H_{21}N$ and $(CHOH.COOH)_2$

Throughout the work on d. Quinidine Tartrates, the water used for making up the solutions, and also for cleaning the glass apparatus employed, was the ordinary laboratory distilled water; but for the work on l. Menthylamine Tartrates, the laboratory distilled water was redistilled, using a silver condenser, and was collected in a Jena glass flask which had previously been carefully cleaned and freed from greasiness.

A/

A fresh supply was prepared daily, and, on the appearance of any sign of greasiness in the flask, it was cleaned with warm chromic acid mixture and then carefully washed out with redistilled water.

The solutions were in every case made up in the following manner. A suitable quantity of the base employed was weighed out, and the amount of acid required to form the normal salt was also weighed out and added to it in a flask supplied with a glass stopper. Water was added, in sufficient quantity to effect complete solution on warming, and finally more water was gradually added until the required weight of solvent was present. The solution was then transferred to a clean dry flask, provided with a well fitting india rubber stopper, and placed in the thermostat until required.

The concentration of a solution is, throughout, taken to be the ratio of the weight of anhydrous salt to the weight of water in the solution.

DENSITY.

The density determinations were made in a Sprengel-Ostwald pyknometer holding about 7 c.c. Before making a determination with the pyknometer, it was washed out several times with alcohol and then repeatedly with water, in both cases with the aid of a water pump, and then thoroughly dried by sucking through it, for about an hour, air first passed through a tower well charged with phosphoric anhydride.

The pyknometer was, at intervals, allowed to stand for a time full of Chromic acid mixture; and, when used for solutions of Quinidine salt, was frequently filled with concentrated HNO_3 and left in the thermostat till any small crystals deposited on the glass had been completely dissolved. Curiously enough, these deposits of small hard crystals were not removed completely by treatment (at least in the cold) with either H_2SO_4, HCl, or Chromic Acid mixture.

The pyknometer was weighed at intervals, empty and also filled to the mark with water at each temperature, and an average value for each of these weights was taken for use in a series of measurements.

Great care was taken in all the density determinations/

determinations to ensure maintenance of a constant temperature in the thermostat.

Values were obtained for the density of the Quinidine salts at 25°, 35° and 50°, and for the Menthylamine salts at 25° and 35°.

The formula usually given for the density of a liquid, referred to that of water at 4°, and corrected for the buoyancy of the air is

$$D_s = \frac{W_s\ D_w}{W_\omega} - \frac{\lambda\ (W_s - W_\omega)}{W_\omega}$$

where D_s represents the corrected density of the solution; D_ω " the density of water at the same temperature;

W_s and W_w the ascertained weights of equal volumes of the solution and of water respectively; and

λ the mean density of the air referred to water at 4° (= .0012)

For the purpose of calculating a long series of values, the formula may be rewritten with advantage thus:-

$$D_s = \frac{W_s}{W_\omega}\ \{\ D_\omega - .0012\ \} + .0012$$

The values of D_ω employed are:-

t	D_W
25°	0·99707
35°	0·99406
50°	0·98807

Thiessen, Scheel and Diesselhorst.

[Landolt - Börnstein: Phys, Chem. Tabellen pp. 27. 29].

I. d. QUINIDINE TARTRATES.

On plotting the values for solutions of the racemate, it appeared clear that the curve representing the series at each temperature was a straight line. For each temperature, then, a straight line was drawn through the extreme racemate values, and its equation was obtained by means of these values. From the equation, values were calculated for each of the concentrations of d. l. and r. salts.

These values were than compared with the results actually obtained by observation [see Table I], and all the observed values were plotted on the diagram, care being taken to distinguish d. l. and r. points by the use of three different signs [see diagram].

By means of Table I, we can compare the density obtained by experiment with the corresponding value taken from the racemate curve (for shortness called the "R" curve). In many cases the values are identical; in the others the difference amounts to only 1 or 2, and in one case to 3, in the fourth place of decimals. It will be observed that in no instance is the actual density of a racemate solution less than the corresponding value taken from the/

TABLE I.

Density (corrected for Air and Water at 4°) at 25°, 35°, and 50° of solutions of d. Quinidine Tartrates, compared with the values of the corresponding concentrations of racemate taken from the "R" curve.

Optical Activity of acid.	Concentration	25°		35°	
		d (found)	d ("R" curve)	d (found)	d ("R" curv
d	·5002	·9985	·9984	·9953	·9953
	·9998	·9994	·9996	–	–
	1·0007	–	–	·9965	·9965
	1·2517	–	–	·9971	·9971
	1·4970	1·0009	1·0008	–	–
	1·8939	–	–	·9987	·9986
	1·9983	1·0022	1·0021	–	–
l.	·4984	·9983	·9983	–	–
	·5041	–	–	·9954	·9953
	·9389	·9996	·9994	–	–
	·9920	–	–	·9963	·9965
	1·4332	–	–	·9976	·9975
	1·4992	1·0009	1·0009	–	–
	1·7463	–	–	·9984	·9983
	1·9238	–	–	·9990	·9987
	1·9263	–	–	–	–
	2·0017	1·0022	1·0021	–	–
	2·1446	–	–	·9993	·9993

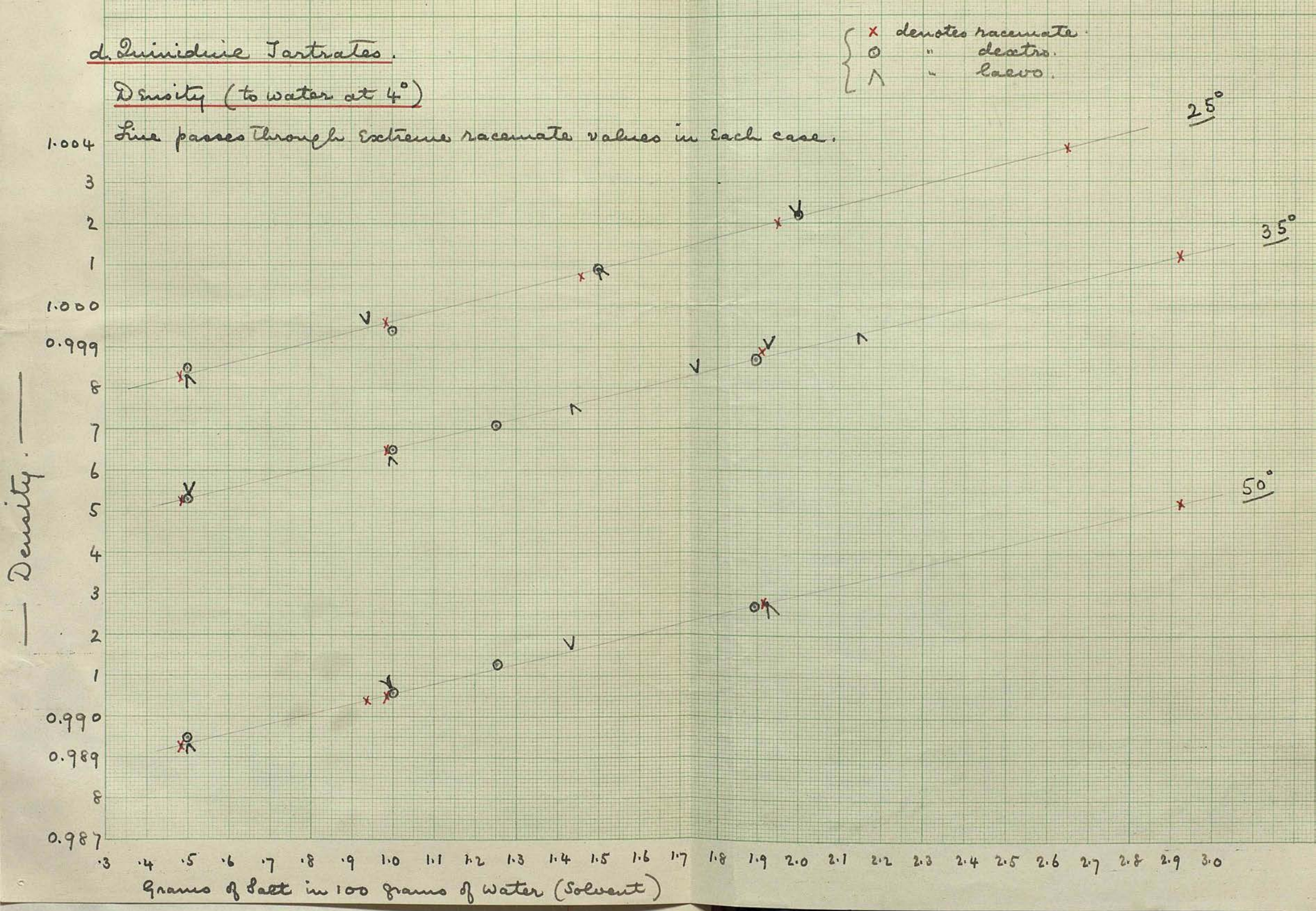
Optical Activity of Acid	Concentration	25°		35°	
		d(found)	d("R"curve)	d(found)	d("R"curve)
r.	·4828	·9983	·9983	·9953	·9953
	·9360	–	–	–	–
	·9842	·9996	·9996	·9965	·9965
	1·4587	1·0007	1·0007	–	–
	1·9137	–	–	·9989	·9987
	1·9514	1·0020	1·0020	–	–
	2·6474	1·0038	1·0038	–	–
	2·9199	–	–	1·0012	1·0012

Optical Activity of Acid	Concentration	50°	
		d (found)	d ("R" curve)
d	·5002	·9895	·9893
	1·0007	·9906	·9905
	1·2517	·9913	·9911
	1·8939	·9927	·9926
l	·5041	·9893	·9893
	·9920	·9907	·9905
	1·4332	·9917	·9915
	1·9263	·9928	·9927
r	·4828	·9893	·9893
	·9360	·9904	·9903
	·9842	·9905	·9905
	1·9137	·9928	·9927
	2·9199	·9952	·9952

d. Quinidine Tartrates.

Density (to water at 4°)

Line passes Through Extreme racemate values in Each case.



the curve: and, with regard to the case alluded to, viz- the density of 1·9238% laevo solution at 35°, where the actual value is greater than the "curve" value by 3 in the fourth place of decimals, it will be observed that the actual density of 1·9137% racemate solution, at the same temperature, ~~solution~~ is greater by 2 in the fourth place than the curve value.

II. 1. MENTHYLAMINE TARTRATES.

In the case of the Menthylamine Tartrates, the racemate curve is not a straight line; but the curvature is very slight, as may be seen by inspection of the diagram.

Table II gives the values obtained by experiment, side by side with the curve values.
It will be noticed that in no case does the actual racemate value differ from the curve value by more than one in the fourth decimal place. Hence the curves may be considered as correctly expressing the values of the function.

The dextro values (with one exception) also agree with the curve values, both at 25° and 35°. Hence we may conclude that the densities of the dextro solutions are identical with those of the racemate solutions of corresponding concentration.

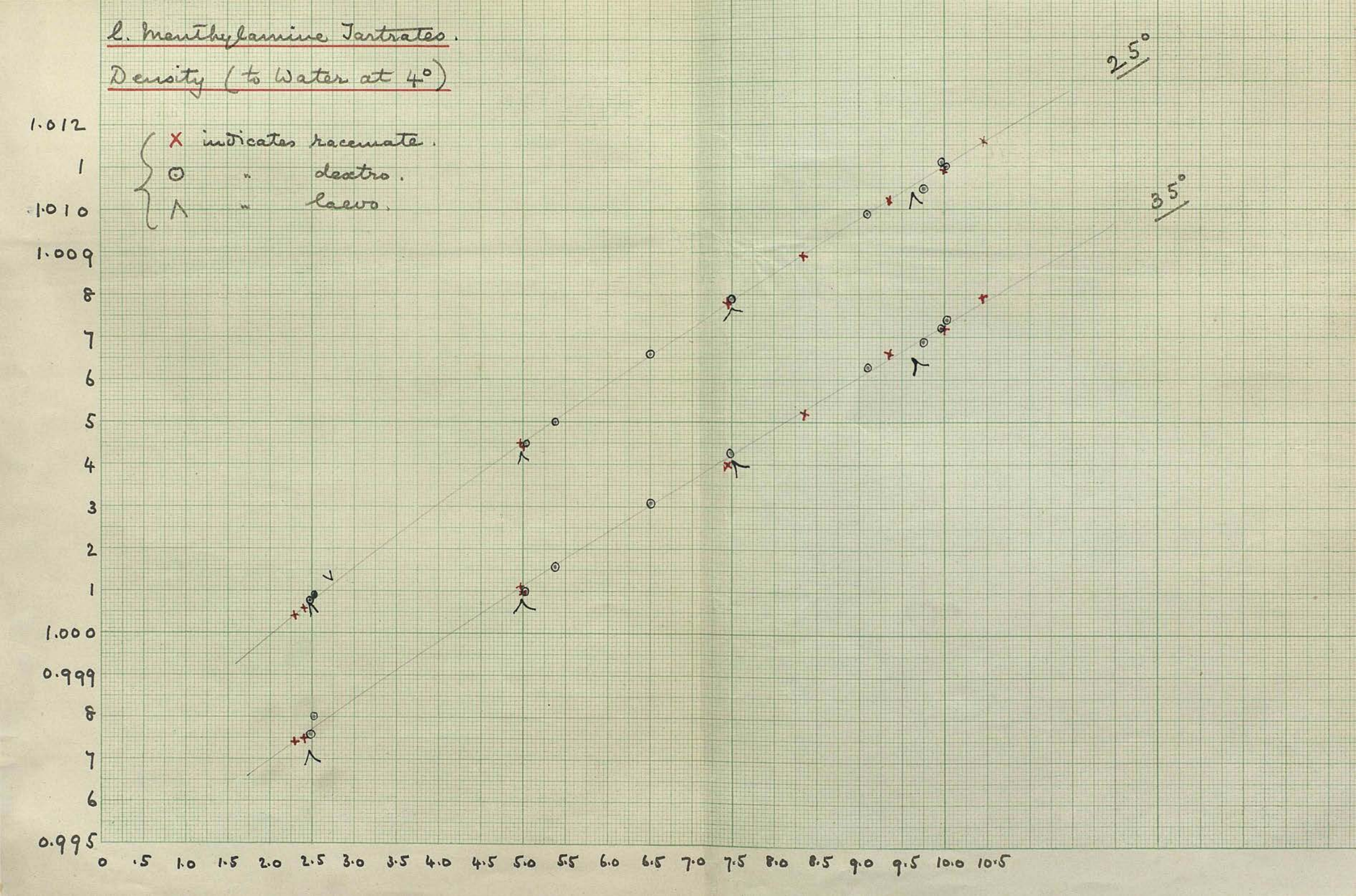
On the other hand, the laevo values seem to differ appreciably/

TABLE II.

Density (corrected for Air and Water at 4°) of solutions of l. Menthylamine Tartrates compared with the values of the corresponding concentrations of racemate taken from the curve - at 25° and 35°.

Optical Activity of Acid.	Concentration.	25°		35°	
		d (found)	d (curve)	d (found)	d (curve)
d.	2·484	1·0008	1·0007	·9976	·9977
	2·5292	1·0009	1·0008	·9980	·9977
	5·0279	1·0045	1·0045	1·0010	1·0011
	5·3733	1·0050	1·0050	1·0016	1·0016
	6·5131	1·0066	1·0066	1·0031	1·0031
	7·492	1·0079	1·0079	1·0043	1·0042
	9·0928	1·0099	1·0099	1·0063	1·0062
	9·5578	1·0105	1·0107	1·0069	1·0069
	9·958	1·0111	1·0110	1·0072	1·0072
	10·023	1·0110	1·0110	1·0074	1·0073
l.	2·469	1·0007	1·0007	·9972	·9977
	2·7376	1·0013	1·0012	-	-
	4·984	1·0043	1·0045	1·0008	1·0011
	7·510	1·0077	1·0079	1·0041	1·0042
	9·637	1·0104	1·0105	1·0065	1·0068

Optical Activity of Acid.	Concentration.	25°		35°	
		d (found)	d (curve)	d (found)	d (curve)
r.	2·2898	1·0004	1·0004	·9974	·9974
	2·394	1·0006	1·0006	·9975	·9975
	4·9793	1·0045	1·0044	1·0011	1·0011
	4·999	1·0044	1·0045	1·0010	1·0011
	7·443	1·0078	1·0078	1·0040	1·0041
	8·3436	1·0089	1·0089	1·0052	1·0052
	9·3463	1·0102	1·0102	1·0066	1·0065
	9·992	1·0109	1·0110	1·0072	1·0073
	10·441	1·0116	1·0116	1·0079	1·0078


l. Menthylamine Tartrates.
Density (to Water at 4°)
× indicates racemate.
⊙ " dextro.
Λ " laevo.
25°
35°
1.012
1
1.010
1.009
8
7
6
5
4
3
2
1
1.000
0.999
8
7
6
0.995
0 .5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5 10.0 10.5

appreciably from the corresponding racemate values. There are nine laevo results, and, of these, 4 agree with the racemate curve values - a difference of one in the fourth place being quite permissable as experimental error. Of the remainder, however, two differ by two, two differ by three, and one differs by five; and in all cases the error is in the same direction, the laevo density being less than that of the corresponding racemate. The differences of 3 and 5 all occur at 35°; and it is noticeable that the divergence from the curve does not increase with the concentration, but is fairly constant, the largest difference indeed occurring at the smallest concentration.

REFRACTIVE INDEX.

The refractive index was obtained by the use of a Zeiss Refractometer, supplied with an arrangement by means of which water from a thermostat may be circulated through the apparatus in order to keep the solution at any required temperature.

I might ~~point out~~ suggest that the weak point of this form of Refractometer is that the thermometer, instead of being actually immersed in the liquid whose refractive index is to be measured - as is done in the older Pulfrich form,- is fixed in a metallic cylinder/

cylinder through which the hot water flows and which is let down into the solution. The observed temperature is thus really that of the hot water and not of the solution. Care therefore has to be taken to ensure that the temperature of the hot water and of the solution are identical, by allowing the water to circulate slowly. The scale of the thermometer, which is cemented through a metal cap screwed on the top of the cylinder, is divided into whole degrees only. I now think that the old Pulfrich form, where the use of a more delicate thermometer is possible - is the better form of instrument, and, with a modification of the cap for the glass cylinder containing the solution to prevent evaporation, and with the employment of a more delicate thermometer than is supplied with the new Zeiss instrument, it would be very much improved.

The method of procedure in determining the refractive index was as follows:-

The thermostat employed to provide the heating water was made by cutting the top off a 13 gallon galvanized iron alcohol drum, and inserting a metal tube with stopcock in the side as low down as possible. This was kept very nearly full of water, and was heated up to about 70° by a large ring burner, the temperature being maintained by the use of a smaller flame.

The/

The hot water was made to circulate through the refractometer for a few minutes, and the solution to be examined was then put in the glass cell and the hot water cylinder lowered into it. The temperature then rose to nearly 70° and was allowed to remain there for quite five minutes. The current of hot water was then turned off, and the temperature allowed to fall slowly.

To prevent layers formimg in the solution, it was from time to time stirred up by raising and lowering the metallic cylinder.

Readings were then taken - by Na light - at intervals of temperature as follows:-

54°, 52°, 50°, 48°, 46°,
37°, 36°, 35°, 34°, 33°,
27°, 26°, 25°, 24°, 23°.

A second set of determinations with a fresh portion of solution was at first frequently made; but subsequently this was not done, as it was found unnecessary.

Readings were taken with water at intervals of time and the differences were very small. An average result for each temperature was employed.

From the observed values, the refractive index was obtained by means of the table supplied with the instrument./

instrument.

The values thus obtained were corrected for water.

Rühlmann's values for the refractive index of water, in air of the same temperature, for Na light (Landolt - Börnstein's phys Chem. Tabellen, p. 670) were taken. Rühlmann gives the values for 20°, 30°, 40°, and 50°. These were plotted on cross-ruled paper, and the values for 25° and 35° were read off :-

t	n^{I}
25°	1·33250
35°	1·33140
50°	1·32906

My own results for water are:-

t	n^{II}
25°	1·33267
35°	1·33134
50°	1·32907

The values of n for the solutions were then corrected as follows:-

$$\text{corrected value of } n \} = \{\text{observed value of } n\} + \{n'_{H_2O} - n''_{H_2O}\}$$

(a) QUINIDINE TARTRATES.

The values of n are given for 25°, 35°, and 50°.

The curve at each temperature is a straight line; and the observed values are set down in Table III side by side with the values taken from the lines on the diagram.

In no case does the observed value differ from the curve value by more than 2 in the fourth place of decimals. It is clear therefore that the values for solutions of d. l. and r. salts of equal concentration, are identical.

(b) MENTHYLAMINE TARTRATES.

The values, when plotted out on diagram paper, indicate that the curves are practically straight lines. The lines are drawn through the extreme racemate values; and those taken from the curves. and Table IV gives both the observed values

On inspecting the diagram, it will be noticed that there are a few deviations from the curve amounting to as much as 3 and 4 in the fourth place of decimals, and, in one instance, ~~to a~~ the difference ~~of~~ to 6. Having regard, however, to what has been said about the difficulty of knowing the exact temperature of the solution at the time of making an observation, I think that these differences may/

may fairly be ascribed to experimental error, and I therefore conclude that the refractive indices of solutions of d. l. and r. salts are identical.

Table III

Refractive Index of Solutions of d. Quinidine Tartrates Compared with the values of the corresponding concentrations of racemate taken from the curve - at 25°, 35° and 50°

Optical Activity of Acid.	Concentration.	25°		35°	
		n (found)	n (curve)	n (found)	n (curve)
d.	·5002	1·3336	1·3336	1·3325	1·3325
	1·0007	1·3347	1·3347	1·3337	1·3336
	1·2517	1·3353	1·3353	1·3342	1·3341
	1·8939	1·3366	1·3367	1·3356	1·3355
l.	·5041	1·3336	1·3336	1·3326	1·3325
	·9210	1·3346	1·3345	1·3335	1·3334
	1·4332	1·3357	1·3357	1·3346	1·3345
	1·7463	1·3364	1·3364	1·3354	1·3352
	1·9263	1·3369	1·3368	1·3358	1·3356
r.	·4985	1·3336	1·3336	1·3325	1·3325
	·9360	1·3345	1·3345	1·3334	1·3334
	1·9137	1·3368	1·3367	1·3356	1·3356
	1·9312	1·3367	1·3368	1·3355	1·3356

Optical Activity of Acid.	Concentration.	50°	
		n (found)	n (curve)
d.	·5002	1·3301	1·3300
	1·0007	1·3312	1·3312
	1·2517	1·3317	1·3317
	1·8939	1·3332	1·3332
l.	·5041	1·3301	1·3300
	·9210	1·3312	1·3310
	1·4332	1·3320	1·3320
	1·7463	1·3329	1·3329
	1·9263	1·3334	1·3333
r.	·4985	1·3300	1·3300
	·9360	1·3312	1·3310
	1·9137	1·3332	1·3333
	1·9312	1·3333	1·3333

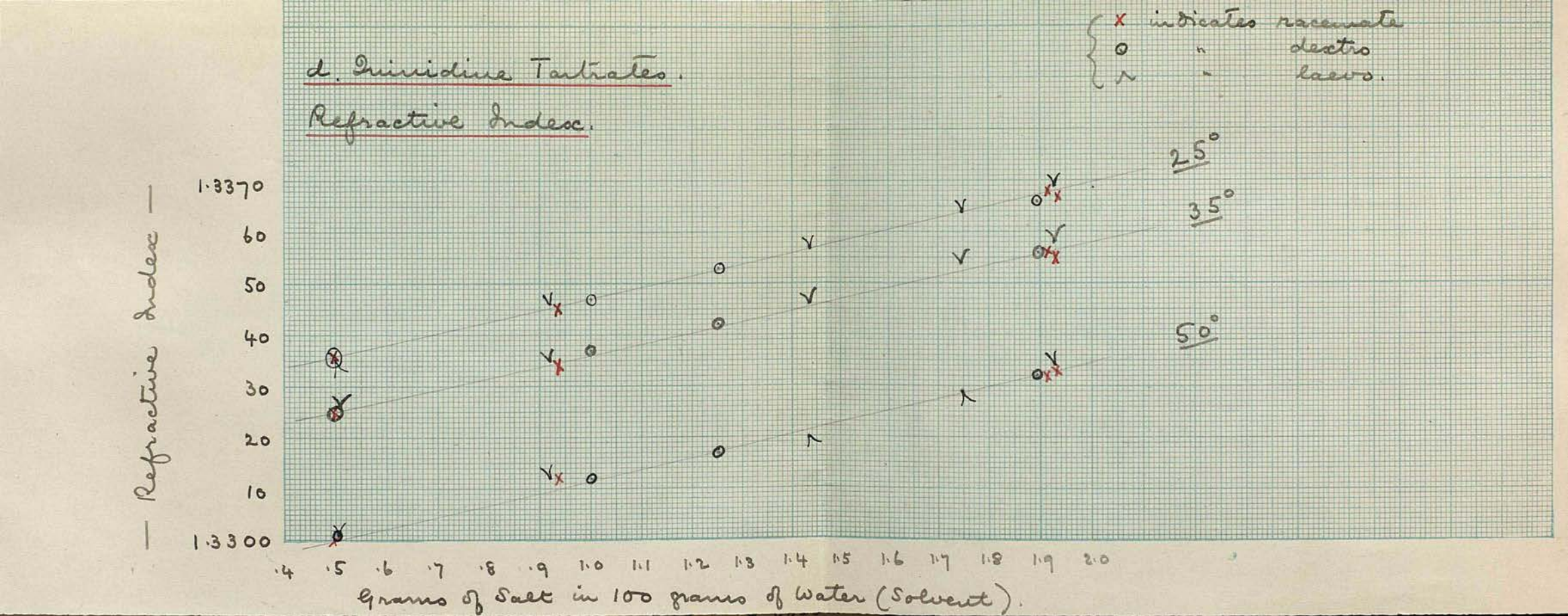

d. Quinidine Tartrates.
Refractive Indexes.
X indicates racemate
O " dextro
Λ " laevo.
25°
35°
50°
— Refractive Index —
1.3370
60
50
40
30
20
10
1.3300
.4 .5 .6 .7 .8 .9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0
Grams of Salt in 100 grams of Water (Solvent).

Table IV.

Refractive Index of Solutions of l. Menthylamine Tartrates compared with the values of the corresponding concentrations of racemate taken from the "R" curve - at 25°, 35° and 50°

Optical Activity of Acid.	Concentration.	25°		35°	
		n (found)	n ("R" curve)	n (found)	n ("R" curve
d	2·529	1·3370	1·3369	1·3359	1·3359
	5·373	1·3418	1·3416	1·3405	1·3405
	6·513	1·3435	1·3435	1·3423	1·3423
	7·492	1·3451	1·3451	1·3440	1·3439
	9·093	1·3478	1·3478	1·3465	1·3465
	9·558	1·3481	1·3485	1·3469	1·3472
	9·759	1·3488	1·3489	1·3476	1·3476
	9·958	1·3492	1·3492	1·3479	1·3479
	10·023	1·3490	1·3493	1·3477	1·3480
l.	2·469	1·3369	1·3368	1·3357	1·3358
	2·738	1·3372	1·3372	1·3360	1·3362
	4·984	1·3412	1·3409	1·3400	1·3399
	7·510	1·3452	1·3451	1·3440	1·3439
	9·637	1·3484	1·3487	1·3470	1·3474

Optical Activity of Acid.	Concentration.	25°		35°	
		n (found)	n ("R" curve)	n (found)	n ("R" curve
r.	2·290	1·3365	1·3365	1·3355	1·3355
	2·394	1·3367	1·3366	1·3357	1·3357
	*(4·979	1·3412	1·3409	1·3400	1·3399)
	4·999	1·3412	1·3410	1·3401	1·3399
	7·158	1·3450	1·3446	1·3437	1·3434
	8·344	1·3466	1·3465	1·3452	1·3453
	9·346	1·3478	1·3482	1·3465	1·3469
	10· 441	1·3500	1·3500	1·3486	1·3486

* Values not plotted on curve, as next values so near.

Optical Activity of Acid.	Concentration.	50°	
		n (found)	n ("R" curve).
d.	2·519	1·3333	1·3333
	5·373	1·3380	1·3377
	6·513	1·3397	1·3395
	7·492	1·3409	1·3410
	9·093	1·3436	1·3434
	9·558	1·3441	1·3442
	9·759	1·3449	1·3445
	9·958	1·3448	1·3448
	10·023	1·3448	1·3449
l.	2·469	1·3330	1·3332
	2·738	1·3335	1·3337
	4·984	1·3371	1·3371
	7·510	1·3412	1·3410
	9·637	1·3441	1·3443

Optical Activity of Acid.	Concentration.	50°	
		n (found)	n ("R" curve).
r.	2·290	1·3330	1·3330
	3·394	1·3331	1·3331
	* (4·979	1·3374	1·3371)
	4·999	1·3375	1·3371
	7·158	1·3411	1·3405
	8·344	1·3426	1·3423
	9·346	1·3439	1·3438
	10·441	1·3455	1·3455

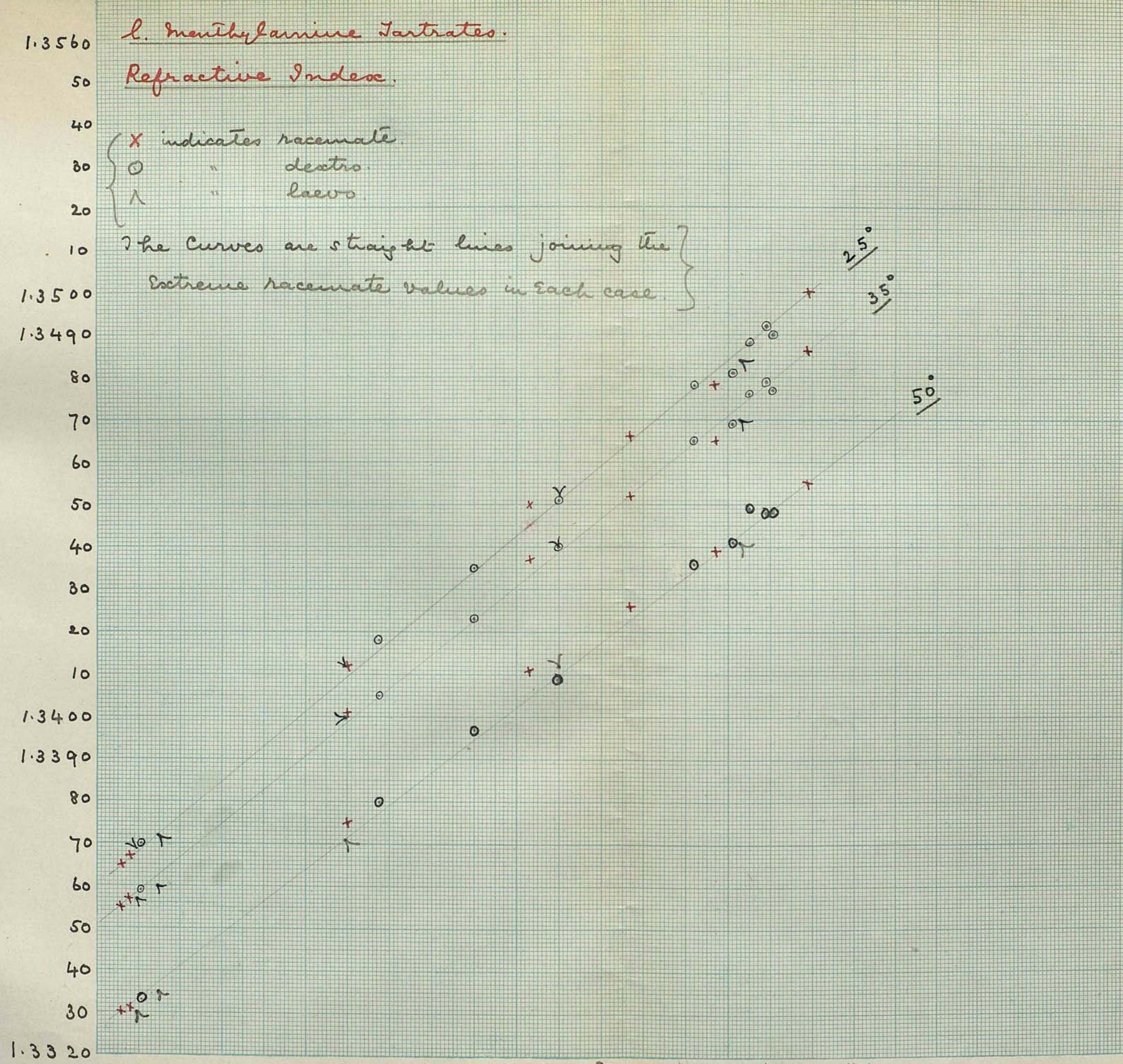
* Value not plotted on curve, as next value so near.

l. Menthylamine Tartrates.

Refractive Index.

× indicates racemate.
⊙ " dextro.
∧ " laevo.

The Curves are straight lines joining the Extreme racemate values in each case.



Grams of Salt in 100 grams of Water (Solvent.)

CONDUCTIVITY.

The Conductivity measurements were made by means of a Wheatstone bridge and telephone, using an alternating current. Two different cells were employed - one of the ordinary Arrhenius pattern - the other a Kohlrausch U shaped cell with narrow connecting tube and large circular electrodes. The resistances employed with the former cell varied from 20 to 100 ohms, and with the latter from 1200 - 2500 ohms, a much sharper minimum being obtained.

The cell constants were obtained by use of m/10 KCl solution. These measurements were made at different times during the progress of the work, and the average readings were employed in calculating the final results.

Measurements of the Conductivity of Solutions of ~~the~~ the l. Menthylamine Tartrate were made at 25° and 35°. For every solution, two or three different resistances were employed, and several readings taken with each. The average of each set of readings was then taken, and the specific conductivity calculated. The results agreed closely, and their mean value was taken as the final result.

The concentration of the solutions ranges from/

from 2·5% to 17·5%.

The racemate values were plotted out and a curve was drawn through them. A very smooth curve was obtained in this way for each temperature. The d. and l. values were then also plotted, and inspection of the diagram shows that there is practically no difference between the values for d. l. and r. solutions.

The specific conductivities of the d. l. and r. solutions are given in Table V.

In Table VI the specific conductivities of the d. and l. solutions (and of one r. solution) are compared with the curve values for corresponding concentrations.

All the racemate values lie on the curve, with the exception of that for 10·105% which is not marked on the diagram, but even in this instance the divergence is negligible.

It is noticeable that the laevo values differ very slightly from those of the racemate at both temperatures, the differences being certainly within the experimental error. On the other hand, the dextro values do not agree so well with those of the racemate, the greatest difference occurring between the values for the 4·713% solution; and it is remarkable that above this concentration the dextro values/

values are all greater than those of the racemate; the divergence however practically disappears at the highest concentration.

I do not think that the differences actually found are of sufficient magnitude to warrant the inference being drawn that the conductivity of the racemate solution is less than that of the dextro solution of equal concentration.

Table V.

Specific Conductivities of solutions of l. Menthylamine Tartrates at 25°

d. Tartrate.

Concentration	K.
2·519	·005695
4·713	·009087
7·492	·01240
9·558	·01420
10·023	·01456
16·824	·01766

l. Tartrate.

2·469	·005626
4·984	·009499
7·510	·01238
9·637	·01418

Racemate

2·394	·005519
4·999	·009574
7·158	·01205
10·105	·01450
10·220	·01461
14·326	·01683
17·621	·01783

Specific conductivities of Solutions of l. Menthylamine Tartrates at 35°

d. Tartrate.

Concentration	K.
2·519	·007083
4·713	·01134
7·492	·01549
9·558	·01781
10·023	·01827
16·824	·02244

l. Tartrate.

2·469	·006989
4·984	·01186
7·510	·01547
9·637	·01778

Racemate.

2·394	·006840
4·999	·01196
7·158	·01503
10·105	·01822
10·220	·01835
14·326	·02128
17·621	·02266

Table VI.

Comparison of the Specific Conductivities, obtained experimentally, of solutions of l. Menthylamine d. Tartrate and l. tartrate (also of one racemate) with the values, deduced from the "R" curve, for corresponding solutions of the racemate.

I. TEMPERATURE 25°.

Optical Activity of Acid.	Concentration	K (found)	K (from "R" curve)
d.	2·519	·00570	·00573
	4·713	·00909	·00918
	7·492	·01240	·01238
	9·558	·01420	·01413
	10·023	·01456	·01447
	16·824	·01766	·01764
l.	2·469	·00563	·00564
	4·984	·00950	·00955
	7·510	·01238	·01239
	9·637	·01418	·01418
r.	10·105	·01450	·01453

II. TEMPERATURE 35°

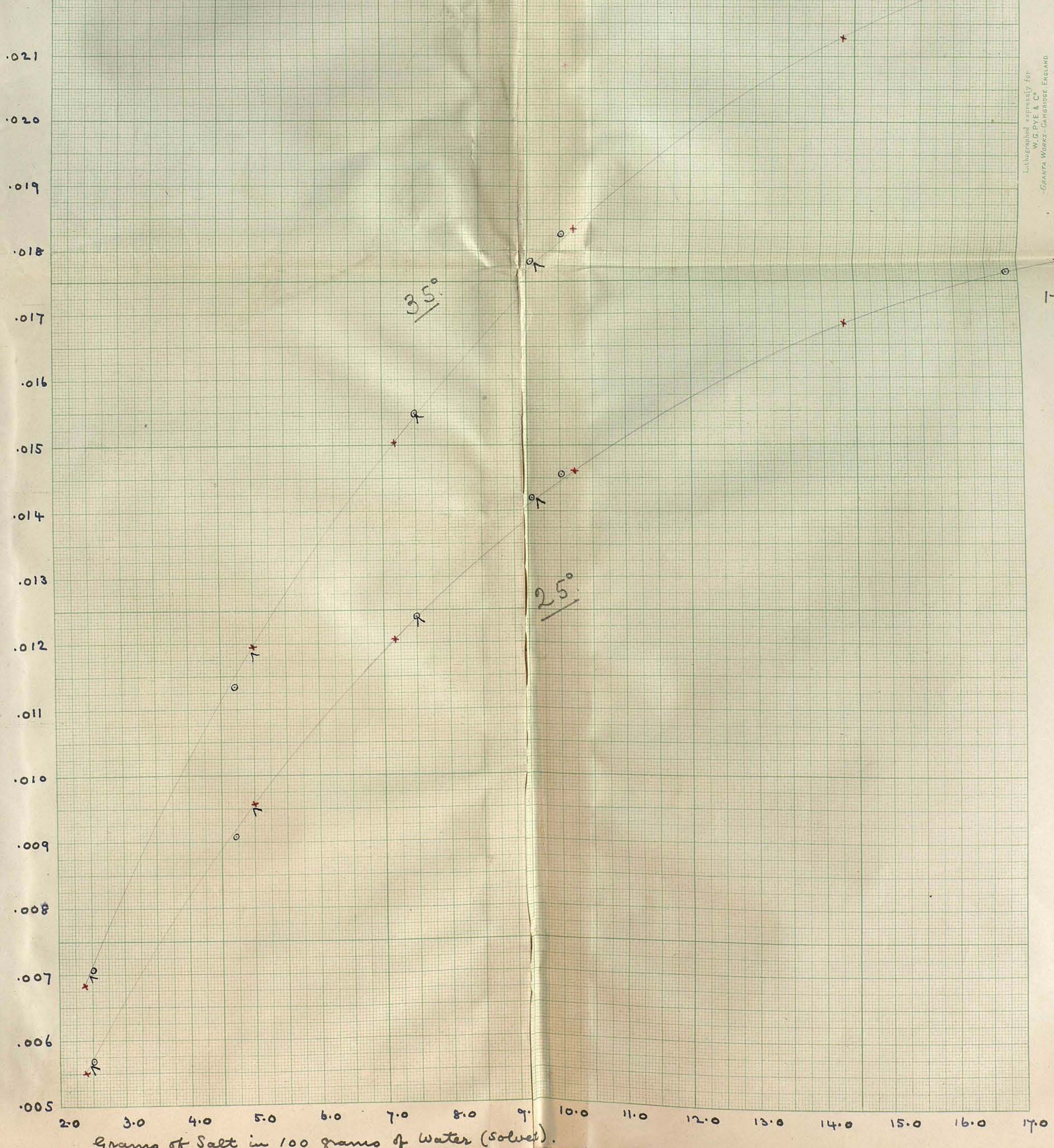
Optical Activity of Acid.	Concentration.	K (found)	K (from "R" Curve)
d.	2·519	·00708	·00713
	4·713	·01134	·01148
	7·492	·01549	·01543
	9·558	·01781	·01771
	10·023	·01827	·01817
	16·824	·02244	·02238
l.	2·469	·00699	·00702
	4·984	·01186	·01195
	7·510	·01547	·01544
	9·637	·01778	·01778
r.	10·105	·01832	·01824

l. Menthylamine Tartrates.

Specific Conductivity of Solutions at 25° - lower curve.
and at 35°. upper curve.

The curves R(25) and R(35) are drawn trough the racemates, & the other values are then plotted down.

× indicates racemate
⊙ " dextro
∧ " laevo.



VISCOSITY.

Measurements of viscosity, at 25° and 35°, were made with solutions of l. Menthylamine Tartrates of concentrations ranging from about 2·5% to slightly over 10%. Two independent determinations were made in respect of every solution, and in no instance was the same capillary tube used for both determinations. Exactly the same volume of liquid was employed on every occasion, the same pipette serving throughout the work.

The viscosity tubes used were of the Poiseuille-Ostwald pattern, and the times of flow for water (at 25°) varied, with the tube used, from about 80 seconds to 152 seconds.

Each tube was once a week, and sometimes more frequently, left over night filled with chromic acid mixture. On the following morning it was emptied, allowed to drain, and the wide limb was washed out repeatedly with water. The whole tube was then completely filled with water, emptied out and allowed to drain. This operation was repeated at least half a dozen times and two or three times after the drainings had ceased to show the acid reaction with litmus paper. Finally, the tube was dried by sucking through it for at least half an hour air previously passed through $CaCl_2$ and P_2O_5./

P_2O_5 Suction was effected by means of a water pump, and, to prevent backward diffusion of water vapour into the tube, a tower containing $CaCl_2$ was placed between it and the pump.

When the tube was thoroughly dry, the time of flow of water was determined; the tube was again dried, and then the time of flow of the solution, whose viscosity was to be measured, was determined. The tube was then cleaned by repeatedly filling it with water and draining, and finally drying it in the manner described above.

The electrically worked chronograph described by Ranken and Taylor (Trans. Roy. Soc. Edin. Vol. XLV., p.397) was employed for accurately recording the times of flow. The speed of the paper was adjusted so that 17 - 20 millimetres corresponded to one ~~record~~ second.

I found that I was enabled to increase materially the accuracy of the time-record by mounting a hand lens of good magnifying power in front of the thermostat, in this way observing the beginning and end of the flow with much greater precision.

The time of flow, whether of water or solution, ~~used~~ in a Viscosity determination is, in every instance, the average of several readings, usually five or more but never less than 3.

The/

The difference between the highest or lowest reading and this average is not more than 1 in 1000.

In many instances I was unable to get concordant readings, and, on every such occasion, the tube was emptied and thoroughly cleaned and dried before the measurement was repeated. I found that, generally speaking, the cause of such irregularities in the time of flow was either

(1) a slight change in the temperature of the thermostat;

(2) slight greasiness in the capillary tube; or

(3) the presence in the capillary tube of a small particle of india rubber, either from the drying apparatus or from the stopper of the flask containing the solution.

As examples of concordant sets of readings I give these:-

Water (25°)	Solution (25°)
121·57 seconds	143·35 seconds
·60	·31
·63	·40
·56	·32
·60	·40
Average 121·59 seconds	143·36 seconds.

The/

The following is the least concordant set of readings used in my determinations:-

Solution (35°)

79·62 seconds.
·50
·44
·44
·46

Average 79·49 seconds.

The relative viscosity of each solution was calculated from each of the two independent measurements: the results agreed with each other very closely, and the mean value was adopted.

As an example of the duplicate measurements, I give those for dextro 9·958% solution at 25°:-

1·4280
1·4279 Taken 1·4280

I select the measurements for this solution, because they were repeated about six months later with the following results:-

1·4271
1·4282 Taken 1·4277

The difference between the two average values is less than 1 in 4,500.

The/

The relative viscosity of the solution to that of water was calculated from the equation—

$$\frac{\eta}{\eta_0} = \frac{t_s \cdot \omega_s}{t_\omega \cdot \omega_\omega}.$$

where η and η_0 represent the absolute viscosity of the solution and of water respectively, at a definite temperature; t_s & t_w represent the time of flow, at the same temperature, of equal volumes of the solution and of water,
and w_s and w_w represent the weight of equal volumes (measured at the same temperature) of the solution and of water.

Tables VII and VIII give the relative and absolute viscosities of the solutions at 25° and 35° respectively.

The values of η in the last column, are obtained from those of η/η_0 by multiplication by the value of η_0 given below the table. (Thorpe and Rodger, Phil. Trans. 185. p.449. 1894).

It will be observed that the relative viscosity diminishes with rise of temperature, and that the difference increases with the concentration of the solution:

thus:-

thus:-

Concentration	Difference. d.	l.	r.
2·394	-	-	·0040
2·469	-	·0091	-
2·484	·0092	-	-
4·984	-	·0183	-
4·999	-	-	·0211
5·028	·0209	-	-
7·492	·0320	-	-
7·510	-	·0307	-
9·636	-	·0409	-
9·759	·0385	-	-
9·958	·0423	-	-
10·220	-	-	·0435

The absolute viscosities (η) of the racemate solutions were plotted for each temperature, and curves were drawn. At 35° the curve goes smoothly through all the values, and at 25° the divergence at any point is extremely slight. The d. and l. values were then also plotted on the diagrams.

In Tables IX and X are given the absolute viscosities (1) obtained by experiment and (2) read off from the "R" curve.

On/

On comparing these results, we find that, at both temperatures, the laevo and racemate values agree with each other very closely. The small differences are sometimes in the one direction and sometimes in the other, and are of the same order of magnitude as the differences between the observed racemate values and those taken from the "R" curve.

At 35° the d. values agree very closely with the corresponding r values; but, at 25°, there are the following differences:-

Concentration.	{"Observed" value.} − {"Curve" value}
2·484	+ ·00004
5·028	+ ·00002
7·492	+ ·00004
9·759	− ·00001
9·958	− ·00002
10·023	+ ·00006

These differences, however, are too irregular to admit of the conclusion being drawn that there is any real difference between the viscosity of the corresponding d. and r. solutions.

Table VII.

VISCOSITY OF SOLUTIONS OF l. MENTHYLAMINE TARTRATES AT 25°.

Optical Activity of Acid.	Concentration	η / η_0	η
d.	2·484	1·0973	·00978
	5·028	1·2031	·01072
	7·492	1·3147	·01171
	9·759	1·4189	·01264
	9·958	1·4280	·01272
	10·023	1·4397	·01283
l.	2·469	1·0948	·00975
	4·984	1·1983	·01068
	7·510	1·3100	·01167
	9·636	1·4106	·01257
r.	2·394	1·0894	·00971
	4·999	1·2005	·01070
	7·443	1·3080	·01165
	9·992	1·4344	·01278
	10·220	1·4428	·01286

η_0 = ·00891 (Thorpe and Rodger).

Table VIII.

VISCOSITY OF SOLUTIONS OF l. MENTHYLAMINE TARTRATES AT 35°

Optical Activity of Acid.	Concentration	η/η_0	η
d.	2·484	1·0881	·00783
	5·028	1·1822	·00851
	7·492	1·2827	·00924
	9·759	1·3804	·00994
	9·958	1·3857	·00998
l.	2·469	1·0857	·00782
	4·984	1·1800	·00850
	7·510	1·2793	·00921
	9·636	1·3697	·00986
r.	2·394	1·0854	·00782
	4·999	1·1794	·00849
	7·158	1·2670	·00912
	10·220	1·3993	·01008

η_0 = ·00720 (Thorpe and Rodger).

Table IX.

Comparison of the Viscosities, obtained experimentally of solutions of l. Menthylamine Tartrates, with the values, deduced from the "R" curve, for corresponding solutions of the racemate.

I. TEMPERATURE 25°.

Optical Activity of Acid.	Concentration	η (found)	η ("R" curve).
d.	2·484	·00978	·00974
	5·028	·01072	·01069
	7·492	·01171	·01167
	9·759	·01264	·01265
	9·958	·01272	·01274
	10·023	·01283	·01277
l.	2·469	·00975	·00973
	4·984	·01068	·01068
	7·510	·01167	·01167
	9·636	·01257	·01259
r.	2·394	·00971	·00971
	4·999	·01070	·01068
	7·443	·01165	·01165
	9·992	·01278	·01276
	10·220	·01286	·01287

Table X.

Comparison of the viscosities, obtained experimentally of solutions of l. Menthylamine Tartrate, with the values, deduced from the "R" curve, for corresponding solutions of the racemate.

II. Temperature 35°.

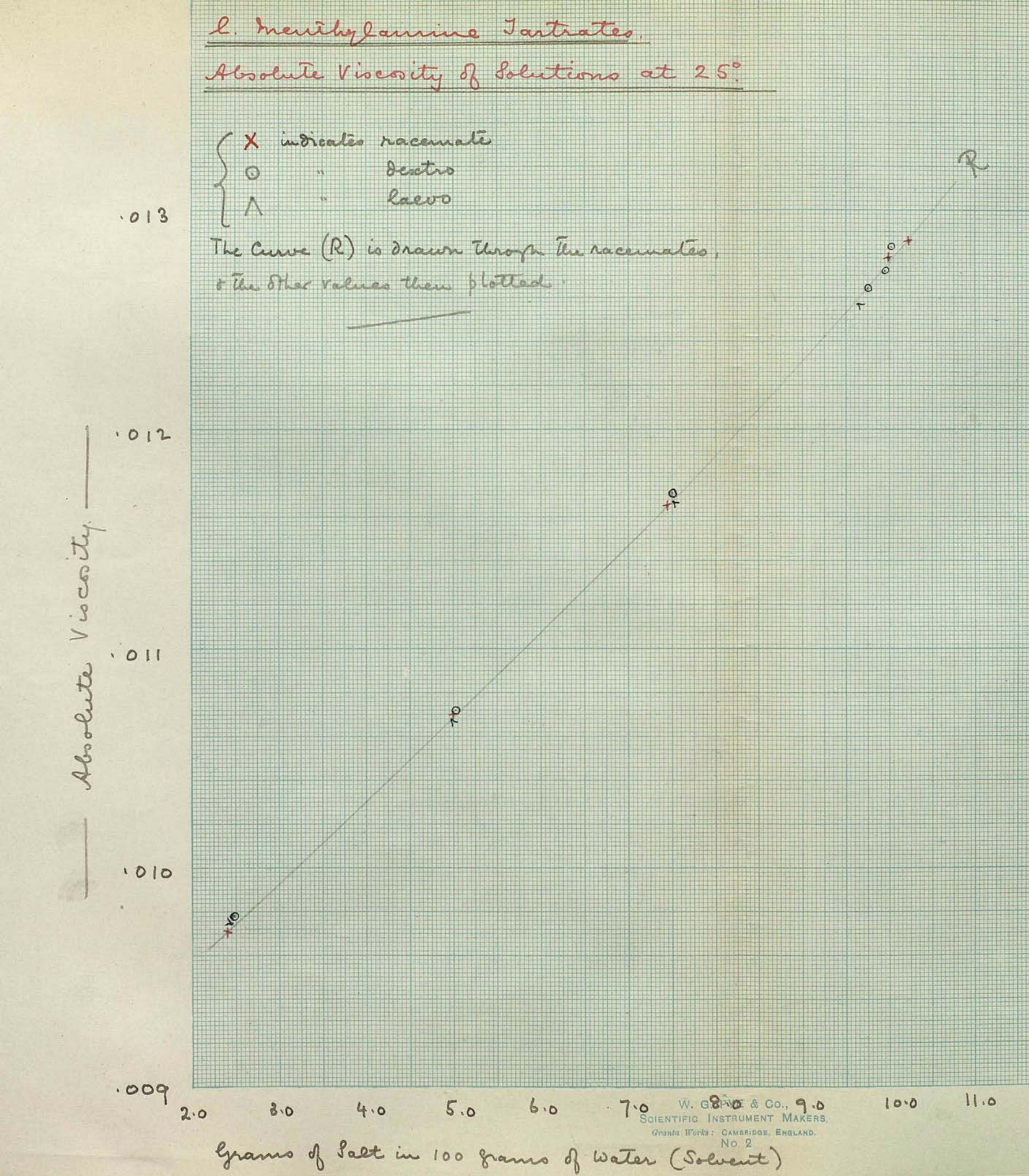
Optical Activity of Acid.	Concentration	η (found)	η ("R" curve)
d.	2·484	·00783	·00784
	5·028	·00851	·00850
	7·492	·00924	·00923
	9·759	·00994	·00993
	9·958	·00998	·00999
l.	2·469	·00782	·00783
	4·984	·00850	·00848
	7·510	·00921	·00922
	9·636	·00986	·00988
r.	2·394	·00782	·00782
	4·999	·00849	·00849
	7·158	·00912	·00912
	10·220	·01008	·01008

l. Methylamine Tartrates.

Absolute Viscosity of Solutions at 25°.

X indicates racemate
⊙ " dextro
Λ " laevo

The Curve (R) is drawn through the racemates, & the other values then plotted.

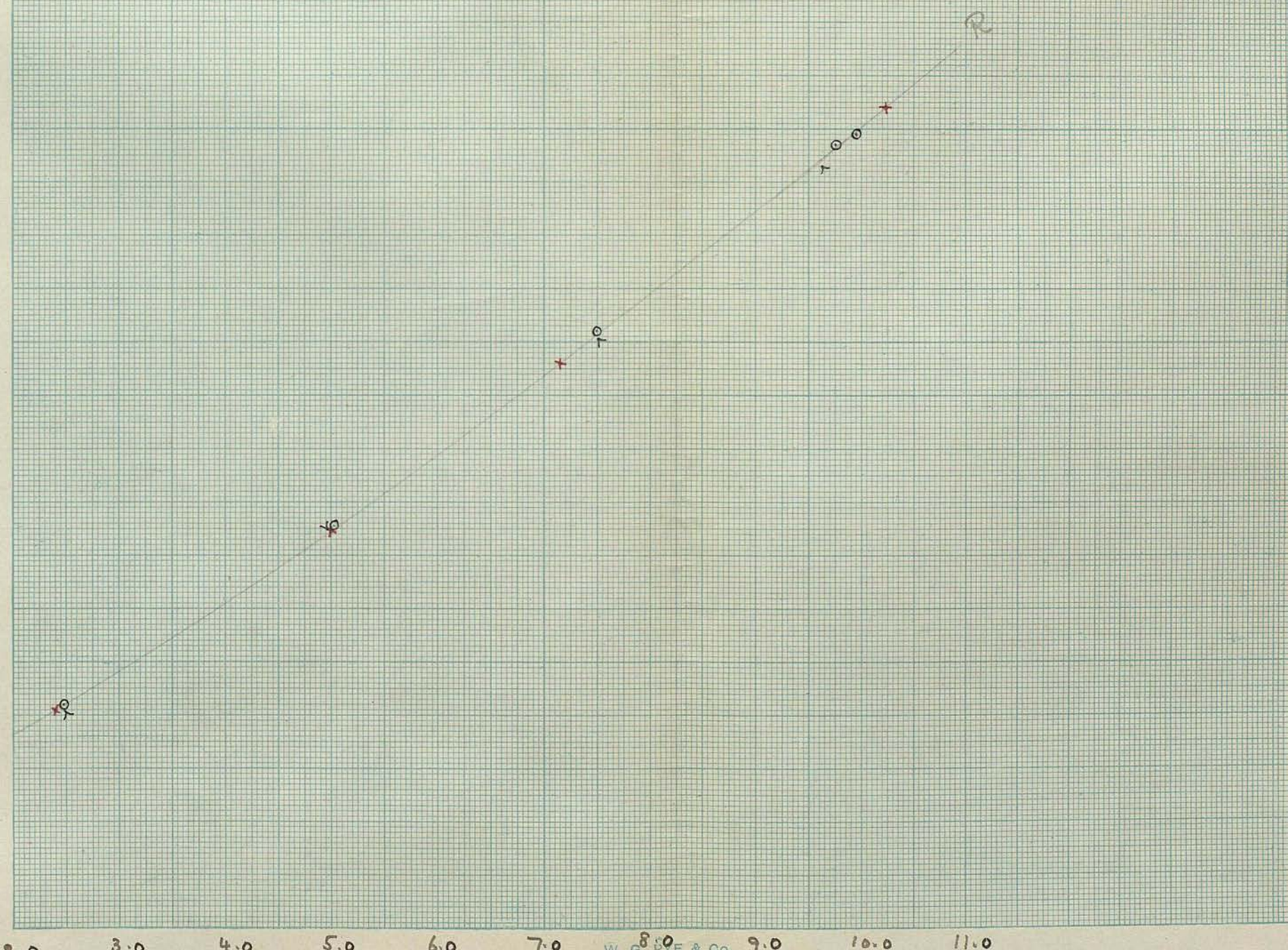


l. menthylamine Tartrates.

Absolute viscosity of Solutions at 35°.

X indicates racemate.
x " dextro.
Λ " laevo.

The curve (R) is drawn through the racemates, & the other values then plotted.



In a paper in the Transactions of the Royal Society of Canada, reprinted in the Chemical News, 1890, Vol.62, pp. 223 etc., Professor J. G. MacGregor discusses the "Variation of the Density with the Concentration of weak aqueous Solutions of certain Salts." The salts considered comprise a series of metallic sulphates and the Hydroxides of Potassium and Sodium. He shows that, within certain limits of concentration, differing to a small extent in the cases of different salts, the densities of dilute solutions of these salts increase in proportion to their concentration, or, in other words, that their concentration - density curves are practically straight lines. He further shows that these lines are nearly equally inclined to the axis of concentrations.

The range of concentration through which the law holds is up to 2% or 3% in the majority of cases, but in the case of Potassium Hydroxide, it holds good up to 5%. (5%)

If D_t and d_t are the densities at the same temperature (t) of a solution and of water respectively, and if p is the "percentage of anhydrous salt in the solution", we have

$$D_t = d_t + Kp.$$

where K is a constant for all sufficiently dilute solutions of the same salt.

The value of K was determined for each salt and the densities obtained by the formula were compared with the corresponding observed values.

From an inspection of the tables furnished in the paper, I find that for concentrations up to 3·5%, the differences between the observed and calculated values vary from zero to 4 or 5 in the fourth place of decimals, while between 3·5% and 5% they vary from 5 in the fourth place to 1 in the third place.

As I had been working with dilute solutions of d. Quinidine and l. Menthylamine Tartrates, and had my results complete before I became aware of Professor MacGregor's paper, it occurred to me that it would be interesting to know how far those results agreed with the corresponding values calculated from the formula. It also occurred to me that a similar law would probably be found to hold for the refractive index of solutions of small concentration.

I. DENSITY.

(a) Quinidine Tartrates.

On referring to the diagram, it will be seen that the assumed racemate curve for each temperature is/

is a straight line passing through the two extreme racemate values. From these two values then, the value of K was obtained, and from this the density values for d. l. and r. solutions were calculated. These are set down to four places of decimals in Table XI, side by side with the observed values. The concentrations vary from ·4828% to 2·9199%. In the last column of the table is set down the difference between the observed and calculated values. In only one case does this amount to as much as 3 in the fourth place of decimals.

The values of d_t will be found on page 15.

Table XI.

Density of Solutions of d. Quinidine Tartrates compared with the values , for the same concentrations, calculated from the formula on page.

25°.

Optical Activity of Acid.	Concentration.	d (found)	d (calculated from formula)	difference.
d.	1·9983	1·0022	1·0021	−0·0001
	1·4970	1·0009	1·0009	−
	·9998	·9994	·9996	+ 0·0002
	·5002	·9985	·9983	− 0·0002
l.	2·0017	1·0022	1·0022	−
	1·4992	1·0009	1·0009	−
	·9389	·9996	·9995	− 0·0001
	·4984	·9983	·9983	−
r.	2·6474	1·0038	1·0038	−
	1·9514	1·0020	1·0020	−
	1·4587	1·0007	1·0008	+ 0·0001
	·9842	·9996	·9996	−
	·4828	·9983	·9983	−

Optical Activity of Acid.	Concentration.	d (found)	d (calculated from formula)	difference.
d.	1·8939	·9987	·9986	- 0·0001
	1·2517	·9971	·9971	-
	1·0007	·9965	·9965	-
	·5502	·9958	·9953	-
l.	2·1446	·9993	·9993	-
	1·9238	·9990	·9987	- 0·0003
	1·7463	·9984	·9983	- 0·0001
	1·4332	·9976	·9975	- 0·0001
	·9920	·9963	·9965	+ 0·0002
	·5041	·9954	·9953	- 0·0001
r.	2·9199	1·0012	1·0011	~~-0·0001~~
	1·9137	·9989	·9987	- 0·0002
	·9842	·9965	·9964	- 0·0001
	·4828	·9953	·9953	~~-0·0001~~

50°

Optical Activity of Acid.	Concentration.	d (found)	d (calculated from formula)	difference.
d.	1·8939	·9927	·9927	–
	1·2517	·9913	·9911	– 0·0002
	1·0007	·9906	·9905	– 0·0001
	·5002	·9895	·9893	– 0·0002
l.	1·9263	·9928	·9927	– 0·0001
	1·4332	·9917	·9915	– 0·0002
	·9920	·9907	·9905	– 0·0002
	·5041	·9893	·9893	–
r.	2·9199	·9952	·9951	– 0·0001
	1·9137	·9928	·9927	– 0·0001
	·9842	·9905	·9905	–
	·9360	·9904	·9903	– 0·0001
	·4828	·9893	·9893	– 0·0001

(b). Menthylamine Tartrates.

In the case of these salts, it will be observed, on referring to the diagram of densities, that the concentrations range from about 2·5% to about 10·5%, and that there is a distinct curvature on the density line, although it is not strongly marked. It will also be noticed that there seems to be a break in the curve about 5%, below which it is almost a straight line.

I have therefore assumed that a straight line passes through the racemate values at 2·2898 and 4·9793 on each curve.

The concentrations included in the scope of the calculations have, however, been extended as high as 5·3733%.

The results obtained from the formula are set down in Table XII, side by side with the observed values, the differences being given in the final column.

In two cases only does the difference exceed 3 in the fourth place of decimals. In each of the two exceptional cases, it will be observed that the difference is comparatively large only at one temperature, and that at the other temperature there is no difference.

Table XII.

Density of Solutions of l. Menthylamine Tartrates compared with the values for the same concentrations, calculated from the formula on page

25°

Optical Activity of Acid.	Concentration.	d (found)	d (calculated from formula)	difference.
d.	2·484	1·0008	1·0009	+ 0·0001
	2·5292	1·0009	1·0009	-
	5·0279	1·0045	1·0047	+ 0·0002
	5·3733	1·0050	1·0053	+ 0·0003
l.	2·469	1·0007	1·0008	+ 0·0001
	2·7376	1·0013	1·0012	- 0·0001
	4·984	1·0043	1·0047	+ 0·0004
r.	2·2898	1·0004	1·0006	+ 0·0002
	2·394	1·0006	1·0007	+ 0·0001
	4·9793	1·0045	1·0047	+ 0·0002
	4·999	1·0044	1·0047	+ 0·0003

Density of Solutions of l. Menthylamine Tartrates compared with the values, for the same concentrations, calculated from the formula on page

35°

Optical Activity of Acid.	Concentration.	d (found)	d (calculated from formula)	difference
d.	2·484	·9976	·9975	- 0·0001
	2·5292	·9980	·9975	- 0·0005
	5·0279	1·0010	1·0010	-
	5·3733	1·0016	1·0015	- 0·0001
l.	2·469	·9972	·9975	+ 0·0003
	4·984	1·0008	1·0009	+ 0·0001
r.	2·2898	·9974	·9972	- 0·0002
	2·394	·9975	·9974	- 0·0001
	4·9793	1·0011	1·0009	- 0·0002
	4·999	1·0010	1·0010	-

It seems clear that, within the limits of concentration employed, the formula of Professor MacGregor correctly represents the density values of the salts used by me.

II. REFRACTIVE INDEX.

If the increase of the density of a dilute salt solution is proportional to the concentration, it seemed not unlikely that a similar rule would be found to hold good for the refractive index of such a solutions.

On referring to the diagrams of the ~~reference~~ refractive index, one sees that the curves are practically straight lines, and it seemed therefore worth while to compare the observed values with those calculated from the equation.

$$n_t = n'_t + Kp$$

Where n_t and n'_t are the refractive indices, at the same temperature, of the solution and of water respectively, p. being the percentage of anhydrous salt in the solution, and K a constant.

The values of n'_t will be found on page 26.

(a) Quinidine Tartrates.

The value of K was obtained from the equation of the straight line passing through the two extreme racemate values. The results are set down, side by side with the observed values, in Table XIII. From the final column, it will be seen that, within the limits of concentration obtaining here, the differences are of practically the same order of magnitude as in the density determinations.

Table XIII.

Refractive Index of Solutions of d. Quinidine Tartrates compared with the values, for the same concentrations, calculated from the formula on page

25°

Optical Activity of Acid.	Concentration.	n (found)	n (calculated from formula)	difference.
d.	·5002	1·3336	1·3337	+ 0·0001
	1·0007	1·3347	1·3347	–
	1·2517	1·3353	1·3352	– 0·0001
	1·8939	1·3366	1·3366	–
l.	·5041	1·3336	1·3337	+ 0·0001
	·9210	1·3346	1·3346	–
	1·4332	1·3357	1·3356	– 0·0001
	1·7463	1·3364	1·3363	– 0·0001
	1·9263	1·3369	1·3367	– 0·0002
r.	·4985	1·3336	1·3336	~~+ 0·0001~~
	· 9360	1·3345	1·3346	+ 0·0001
	1·9137	1·3368	1·3367	– 0·0001
	1·9312	1·3367	1·3367	~~+ 0·0001~~

35°

Optical Activity of Acid.	Concentration.	n(found)	n (calculated from formula)	difference.
d.	·5002	1·3325	1·3325	–
	1·0007	1·3337	1·3335	– 0·0002
	1·3517	1·3342	1·3340	– 0·0002
	1·8939	1·3356	1·3354	– 0·0002
l.	·5041	1·3326	1·3325	– 0·0001
	·9210	1·3335	1·3333	– 0·0002
	1·4332	1·3346	1·3344	– 0·0002
	1·7463	1·3354	1·3351	– 0·0003
	1·9263	1·3358	1·3355	– 0·0003
r.	·4985	1·3325	1·3325	–
	·9360	1·3334	1·3334	–
	1·9137	1·3356	1·3354	– 0·0002
	1·9312	1·3355	1·3355	–

50°

Optical Activity of Acid.	Concentration.	n (found)	n (calculated from formula)	difference.
d.	·5002	1·3301	1·3302	+ 0·0001
	1·0007	1·3312	1·3314	+ 0·0002
	1·2517	1·3317	1·3320	+ 0·0003
	1·8939	1·3332	1·3334	+ 0·0002
l.	·5041	1·3301	1·3302	+ 0·0001
	·9210	1·3312	1·3312	–
	1·4332	1·3320	1·3324	+ 0·0004
	1·7463	1·3329	1·3331	+ 0·0002
	1·9263	1·3334	1·3335	+ 0·0001
r.	·4985	1·3300	1·3302	+ 0·0002
	·9360	1·3312	1·3312	–
	1·9137	1·3332	1·3335	+ 0·0003
	1·9312	1·3333	1·3335	+ 0·0002

(b) Menthylamine Tartrates.

As in the case of densities, so here I restricted the scope of investigation to concentrations less than 5%. The values of K are obtained by means of the equations involving the refractive indices of the racemate solutions of concentrations 2·2898% and 4·9990%. The calculated refractive indices are set out in Table XIV, together with the observed values, and the differences, as before. Further, in order to test the assumption that the rule would not hold over, say 5%, I have put down the values, obtained from the same constants, at 25°, for three solutions of dextro salt of concentrations between 5% and 10%, and it will be seen that the differences are considerably greater than in the case of more dilute solutions. In the latter case, on the other hand, the differences are very small and of the same order as in the case of the Quinidine salts.

It is clear therefore that for solutions of less concentration than 5% the assumed law holds good.

Table XIV

Refractive Index of Solutions of l. Menthylamine Tartrates compared with the values for the same concentrations, calculated from the formula on page

25°

Optical Activity of Acid.	Concentration.	n (found)	n (calculated from formula)	difference
d.	9·958	1·3492	1·3498	+ 0·0006
	9·0928	1·3478	1·3483	+ 0·0005
	7·492	1·3451	1·3456	+ 0·0005
	5·3733	1·3418	1·3421	+ 0·0003
	2·5292	1·3370	1·3369	- 0·0001
l.	4·984	1·3412	1·3412	-
	2·7376	1·3372	1·3373	+ 0·0001
	2·469	1·3369	1·3368	- 0·0001
r.	4·999	1·3412	1·3412	-
	4·9793	1·3412	1·3412	-
	2·394	1·3367	1·3367	-
	2·2898	1·3365	1·3365	-

35°.

Optical Activity of Acid.	Concentration	n (found)	n (calculated from formula)	difference
d.	5·3733	1·3405	1·3405	-
	2·5292	1·3359	1·3357	- 0·0002
l.	4·984	1·3400	1·3399	- 0·0001
	2·7376	1·3360	1·3361	+ 0·0001
	2·469	1·3357	1·3356	- 0·0001
r.	4·999	1·3401	1·3401	- 0·0002
	4·9793	1·3400	1·3399	- 0·0001
	2·394	1·3357	1·3355	- 0·0002
	2·2898	1·3355	1·3353	- 0·0002

50°

Optical Activity of Acid.	Concentration	n (found)	n (calculated from formula)	difference.
d.	5·3733	1·3380	1·3381	+ 0·0001
	2·5292	1·3333	1·3333	–
l.	4·984	1·3371	1·3374	+ 0·0003
	2·7376	1·3335	1·3336	+ 0·0001
	2·469	1·3330	1·3332	+ 0·0002
r.	4·999	1·3375	1·3374	– 0·0001
	4·9793	1·3374	1·3374	–
	2·394	1·3331	1·3331	–
	2·2898	1·3330	1·3329	– 0·0001

the terms

With regard to "concentration" in Professor MacGregor's paper, I infer that it stands for the ratio of anhydrous salt to solution, but this is ~~is~~ not stated definitely. My concentrations are all taken as the ratio of anhydrous salt to water.

Finally with regard to the value of K, Professor MacGregor states that, in the case of all the salts he deals with in his paper, the value of K does not vary greatly. The extreme values taken from his table are .00816 and .01456.

by me

The values of K obtained ~~zinc~~ in the case of Quinidine and menthylamine Tartrates are very much smaller than those and are as follows:-

(1) $D_t = d_t + Kp$

t.	Quinidine $\bar{T}$.	Menthylamine $\bar{T}$.
25°	.002541	.001524
35°	.002421	.001376
50°	.002421	-

(2) $n_t = n'_t + Kp$

t	Quinidine $\bar{T}$.	Menthylamine $\bar{T}$.
25°	.002185	.001742
35°	.002108	.001702
50°	.002317	.001676

From/

From these values of K, and by inspection of the diagrams, it is clear that the straight lines representing the densities and refractive indices respectively, of the dilute solutions discussed here, are practically equally inclined to the axis of concentrations, and in this respect also the solutions I have dealt with agree in their behaviour with those discussed by Professor MacGregor.

The result of this investigation may be briefly summed up to the effect that I have not found any differences in the physical properties of aqueous solutions of the optically active and racemic forms of Tartaric acid in presence of the optically active bases employed.

My best thanks are due to Dr. Taylor for advice in connection with this research; and also to Professors Crum Brown and Walker for granting me facilities to carry it out, and for the kindly interest that they have manifested in the progress of the work.
